SANDIA NATIONAL LABORATORIES
WASTE ISOLATION PILOT PLANT
CHEMICAL AND DISPOSAL ROOM PROCESSES DEPARTMENT 6748

TECHNICAL OPERATING PROCEDURE (TOP)
TOP-544

PREPARING SYNTHETIC BRINES FOR CHEMICAL-RETARDATION AND TRANSPORT EXPERIMENTS

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1.0 INTRODUCTION, PURPOSE, AND SCOPE

1.1 Introduction

In support of the WIPP project, laboratory tests are required to evaluate retardation of dissolved and colloidal actinides in the Culebra Dolomite and to evaluate colloid-facilitated transport of actinides in the WIPP disposal room and in the Culebra Dolomite. Some of these tests are empirical experiments, designed to simulate conditions in the subsurface geochemical environment. In these tests, it is desirable to use synthetic brines with compositions similar to the compositions of naturally occuring brines from the WIPP Site.

1.2 Purpose and Scope

This procedure gives recipes for a variety of synthetic brines and tells how to prepare them in both small (≤2 L) and large (>2 L) quantities.

Synthetic brines are used in various chemical-retardation and transport experiments being done in support of the WIPP project. Synthetic brines used in the experiments shall be prepared in accordance with this procedure.

2.0 RESPONSIBILITIES

2.1 Principal Investigator

The principal investigator shall determine the requirements for each batch of brine including which recipe to use, the amount to prepare, and whether to equilibrate the brine with rock.

2.2 Lab Personnel

Personnel who prepare synthetic brines shall comply with the requirements of this procedure.

3.0 SAFETY

Safety issues associated with preparing synthetic brines are covered in Safe Operating Procedures for the facilities in which the brines will be prepared. These include, but are not limited to, the Water-Chemistry Laboratory in 823/2079 (SP472968) and the Colloid- and Surface-Chemistry Laboratory in 823/B45 (SP472799).

4.0 DEFINITIONS

Charge balance error -groundwaters (including brines) are electrically neutral. That is, the sum of the positive ionic charges equals the sum of the negative ionic charges. The **charge balance error** is a measure of the apparent deviation from electrical neutrality. The charge balance error may be caused by errors in the reported concentrations of the solutes, by important ionic species not being included in the calculation, or by both.

The charge-balance equation may be written as follows:

$$CBE = \frac{\Sigma cations - \Sigma anions}{\Sigma cations + \Sigma anions} \times 100$$

Where CBE = charge balance error (percent)
Σcations = sum of the positive ionic charges
Σanions = sum of the negative ionic charges

5.0 RECIPES

Section 5.1 discusses recipes for the synthetic Culebra brines used in chemical retardation experiments, colloid research, and solubility research. Section 5.2 describes a method for formulating a recipe from a given bulk composition.

5.1 Culebra Brines

Six synthetic brines are being used that have bulk compositions similar to naturally occuring brines from the Culebra Dolomite. Tables 1, 2, and 3 give the recipes for and compositions of the AISinR brine (from Nitsche et al., 1992, p. 11-13), the H-17 Brine (from Nitsche et al., 1994), and the VPX brines (VPX25, VPX26, VPX27, and VPX28; from Lucero et al., 1995).

5.2 Formulating a Recipe

Keep the following points in mind when formulating a recipe.

- The composition of the brine being simulated must be appropriate for the experiment. The Principal Investigator will specify the appropriate composition.
- The recipe must give the desired composition. This can be verified by calculating the composition of the brine that will be produced by following the recipe.

In many cases, the measured composition of the brine being simulated will not have a charge balance error of zero. In such cases, it will be impossible to generate a recipe that produces that exact composition. If the charge-balance error is not zero, there are several ways to proceed. Two possibilities are given here.

- Adjust the concentrations of any or all of the solutes so that the composition has a charge balance error of zero. Then follow steps 1 through 5 below.
- Allow the most abundant cation and anion (typically Na and Cl) to share the discrepancy. Follow steps 1 through 5 below, and recognize that the amount of NaCl needed to provide the remaining Na and the amount needed to proved the remaining Cl may may differ significantly. As instructed in step 5, use the average of the two amounts.

The following steps summarize how to formulate a recipe.

1) Select simple reagents. For example, add potassium as either the chloride or the sulfate salt, rather than some of each. If the reagents are selected carefully, only Na, Cl, and perhaps sulfate will be contributed by more than one reagent, and the calculations will be simpler.

2) Start with a solute that will be contributed by only one reagent (such as B, Br, inorganic carbon, Ca, K, or Mg). Calculate the amount of reagent needed to provide the desired amount of that solute.

3) Repeat step 2 for each solute that will be contributed by only one reagent.

4) If sulfate is being contributed by more than one source, calculate the amount provided for in steps 2 and 3, and then calculate the amount of Na_2SO_4 needed to make up the difference.

5) Calculate the amounts of Na and Cl provided for in steps 2, 3, and 4. Then calculate the amount of NaCl needed to provide the remaining sodium. Calculate separately the amount needed to provide the remaining chloride. Note that even if the composition had a charge balance error of zero, the two numbers may differ slightly because of round-off errors. Use the average of the two numbers.

Be aware that the preceding discussion applies to brines in which sodium and chloride are the dominant solutes (from the vicinity of the WIPP Site). If other groundwaters from the region are to be simulated, additional solutes may be of interest (such as strontium or nitrate) and other solutes (such as calcium and sulfate) may be important. The procedure for formulating a recipe can be adjusted accordingly.

For information about how to calculate the concentrations of the various solutes, consult an introductory chemistry textbook or technician's handbook such as the Chemical Technicians' Ready Reference Handbook (Shugar and Ballinger, 1990).

6.0 EQUIPMENT AND REAGENTS

6.1 EQUIPMENT

6.1.1 Equipment for Drying Reagents

Equipment for drying reagents includes glassware (weighing bottles or beakers), a laboratory oven, desiccators, and desiccant.

6.1.2 Equipment for Weighing Reagents

Equipment for weighing reagents includes glass or plasticware (disposable weighing boats, weighing bottles, or beakers), spatulas, an analytical balance (readable to at least 0.0001 g), and standard weights (for performance checks).

6.1.3 Miscellaneous Labware

Additional equipment includes beakers, watch glasses, stirring equipment (stir plates, stirrers, stir-bar remover), hot plates, class-A volumetric flasks, plastic bottles or carboys, sieves,

filtering equipment (vacuum pump, membranes, membrane holders), adjustable pipets, and pH measuring equipment (electrodes, meter).

6.2 REAGENTS AND CORE

6.2.1 Solids

Inorganic salts and other solids (such as boric acid) are used to prepare the brine.

- Use ACS reagent grade solids whenever possible.
- Record in the scientific notebook details about the solids used including the manufacturer, the grade, the part number, the lot number, and the expiration date (if any).

6.2.2 Acid and Base Solutions

Hydrochloric acid and sodium hydroxide are sometimes used to adjust the pH of the brine.

- Use high purity concentrated hydrochloric acid whenever possible.
- Use a commercially prepared NaOH solution, or prepare a solution by dissolving reagent grade NaOH in demineralized water. In most cases a concentrated solution (≥10 N) will be appropriate.
- Record in the scientific notebook details about the hydrochloric acid and sodium hydroxide used including the manufacturer, the grade, the concentration, the part number, the lot number, and the expiration date (if any).

6.2.3 Water

Unless the Principal Investigator requests something else, use demineralized water.

- Record in the scientific notebook details about the water. If it was purified in the lab, include information about the method (such as deionized or distilled), the equipment used, and the purity (specific conductance or resistance). If it was purchased, include information about the manufacturer as well as the method and purity.

6.2.4 Deuterated Water

If the Principal Investigator specifies that a brine be prepared using deuterated water (D_2O), do the following.

- Record in the scientific notebook details about the water including the manufacturer, the purity, the part number, and the lot number.
- Substitute deuterated water for demineralized water in the steps in section 7.5.

6.2.5 Core

The Principal Investigator may specify that the synthetic brine be equilibrated with rock.

- Get the appropriate core from the Principal Investigator or designee.

- Record in the scientific notebook details about obtaining the core. These details should include, but are not limited to, the core identification number, when and from whom it was received, and a brief description including the quantity.

7.0 PROCEDURE FOR PREPARING BRINE

7.1 Summary

Preparing a synthetic brine involves dissolving the appropriate quantities of reagents in water; diluting to the appropriate volume; equilibrating with crushed rock, if necessary; filtering; and adjusting the pH.

Record all your work in the scientific notebook.

7.2 Preliminary Steps

Get the requirements for the brine from the Principal Investigator -- which recipe is to be used, the final pH (if not specified in the recipe), the amount required, whether or not the brine is to be equilibrated with rock (and if so, what size fraction).

> Note: if the volumn is ≤2 L, it must correspond to the volume of a Class-A volumetric flask. If the volumn is >2 L, it should be a multiple of 2 liters.

Calculate the amounts of the reagents that will be needed. The recipes specify the amounts needed for one liter of brine. For each reagent, the mass needed is the mass specified in the recipe multiplied by the number of liters of brine to be prepared.

Ensure that adequate amounts of reagents are available.

If the brine is to be equilibrated with rock, ensure that the rock is available.

7.3 Drying the Reagents

Dry the anhydrous salts in the laboratory oven at 105 to 110 °C for at least four hours (longer for large quantities). Record the details about the drying in the scientific notebook.

Store the dried salts in a desiccator.

Do **not** dry sodium bicarbonate ($NaHCO_3$) because it may begin decomposing to sodium carbonate (Na_2CO_3) when heated.

Do **not** dry hydrated salts because they will begin to lose their water of hydration when heated above 100 °C.

7.4 Weighing the Reagents

Comply with the requirements of TOP-542 (Calibration, Use, and Maintenance of Balances).

If a reagent is to be used immediately, weigh it into a clean, appropriately sized plastic or glass container (weighing boat or beaker) from which the reagent can be quantitatively transferred.

If a reagent is to be used later, weigh it into a clean, appropriately sized plastic or glass container that can be covered (for example, with parafilm, a watchglass, or a lid) and from which the reagent can be quantitatively transferred.

Record the details about the weighing in the scientific notebook. Include information about the balance calibration and performance check.

7.5 Dissolving the Reagents and Adjusting the Volume

The procedure will vary depending on several factors. For example, up to two liters of brine may be prepared in a volumetric flask; larger quantities require some other method for reaching the desired volume. Brines that are close to saturated with the major constituents are difficult to prepare volumetrically and require special steps and additional time.

Sections 7.5.1 and 7.5.2 describe methods that are suitable for preparing synthetic brines that are not close to saturated with sodium chloride. Deviations from these methods are acceptable if the following conditions are met:

- Known (weighed) amounts of the appropriate reagents are dissolved in the final brine.
- The requested volume of brine is prepared.
- Independent checks of the composition of the brine verify the composition.
- Details about the preparation are recorded in the scientific notebook

7.5.1 Synthetic Brines -- ≤2 L

If sodium tetraborate (hydrous or anhydrous) is included, quantitatively transfer it to a glass beaker. To ensure that all the sodium tetraborate is transferred, rinse the weighing container with at least three aliquots of demineralized water, each time adding the rinsings to the beaker. Add sufficient demineralized water to dissolve the salt. Add a magnetic stir bar. Cover the beaker. Place the beaker on a stir plate and stir at the lowest speed possible until all the sodium tetraborate has dissolved. It will take several hours or overnight for the sodium tetraborate to dissolve. Remove the stir bar, and rinse it with demineralized water, each time adding the rinsings to the solution.

Prepare a second solution using the remaining salts. Quantitatively transfer the first salt to a glass beaker. To ensure that all the salt is transferred, rinse the weighing container with at least three aliquots of demineralized water, each time adding the rinsings to the beaker. Add sufficient demineralized water to dissolve the salts. Add a magnetic stir bar, and cover the beaker. Place the beaker on a stir plate, and stir at the lowest speed possible until all the salt has dissolved.

Add the next salt, taking care to transfer it quantitatively, and stir until it is dissolved. Continue adding and dissolving the salts one at a time until all have been added and dissolved. Then remove the stir bar, and rinse it with demineralized water, each time adding the rinsings to the solution.

Pour the sodium tetraborate solution into an appropriately sized, clean, class-A volumetric flask. Rinse the beaker at least three times with small aliquots of demineralized water to ensure that all the solution is transferred, each time adding the rinsings to the flask.

Add the solution containing the other salts to the volumetric flask. Rinse the beaker at least three times with small aliquots of demineralized water to ensure that all the solution is transferred, each time adding the rinsings to the flask.

Adjust the volume with demineralized water, mix thoroughly, and transfer the solution to a clean, labeled plastic bottle.

7.5.2 Synthetic Brines -- >2 L

If sodium tetraborate (hydrous or anhydrous) is included, dissolve it as described in section 7.5.1. Using the remaining salts, prepare a second solution as described in section 7.5.1.

Pour the sodium tetraborate solution into a clean, two-liter, class A volumetric flask. Rinse the beaker at least three times with small aliquots of demineralized water to ensure that all the solution is transferred, each time adding the rinsings to the flask.

Add some of the solution containing the other salts to the volumetric flask, stopping when the 2-L mark on the neck of the flask is reached. Pour the contents of the flask into a clean plastic bottle or carboy, allowing the flask to drain as completely as possible.

Pour some more of the solution containing the other salts into the volumetric flask, stopping when the 2-L mark on the neck of the flask is reached. Add the contents of the flask to the plastic bottle or carboy, allowing the flask to drain as completely as possible.

Repeat the preceding step until all of the salt solution has been transferred. Rinse the beaker at least three times with small aliquots of demineralized water to ensure that all the solution is transferred, each time adding the rinsings to the flask. Adjust the volumn to 2 L with demineralized water and transfer the solution to the plastic bottle or carboy, allowing the flask to drain as completely as possible.

Use the same volumetric flask to measure and add 2-L quantities of demineralized water, each time allowing the flask to drain as completely as possible, until the desired total volume is reached.

Mix the contents of the bottle or carboy thoroughly.

7.6 Equilibrating with Crushed Rock

Grind the rock with a mortar and pestle. Use sieves to obtain the size fraction specified by the Principal Investigator. Re-grind material that is too coarse. Discard or archive material that is too fine. Record details about the grinding and sieving (including the sieve size) in the scientific notebook.

Add the ground rock to the brine. Equilibrate for the amount of time specified by the Principal Investigator. Record details about the equilibration in the scientific notebook.

7.7 Filtering Brine

Filter the solution through filter paper or a membrane as specified by the Principal Investigator. Record details about the filtering and filter apparatus (including the membrane type and pore size) in the scientific notebook.

Store the solution in clean, labeled plastic bottles or carboys.

7.8 Adjusting the pH

Comply with the requirements of TOP-535 (Calibration, Use, and Maintenance of pH Meters and Probes). Check the pH. Adjust it with HCl or NaOH solution as appropriate. Record details about adjusting the pH in the scientific notebook.

7.9 Verifying the Composition

Find out from the Principal Investigator which solutes are to be verified. Use appropriate analytical techniques (such as IC or ICP) to measure the concentrations of the selected solutes. Comply with the requirements of the appropriate TOPs for specific instruments and equipment (such as the IC, ICP, and the adjustable pipets). (TOPs currently available are included in the reference list in section 9.0.) Record details about the analyses in the scientific notebook

8.0 QA RECORDS

8.1 Scientific Notebooks

When using scientific notebooks, comply with the requirements of QAP20-2 (Preparing, Reviewing, and Approving Scientific Notebooks). In addition to recording all information required in sections 6 and 7, record in the scientific notebook any deviations from this procedure.

9.0 REFERENCES

Lucero, D. A., Gelbard, F., Behl, Y. K., and Romero, J. A. (1995, in review), Test plan for laboratory column experiments for radionuclide adsorption studies of the Culebra Dolomite Member of the Rustler Formation at the WIPP Site, Sandia National Laboratories, Albuquerque, New Mexico.

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QAP5-3, Preparing, Reviewing, and Approving Technical Operating Procedures (TOPs), rev. 1, 07/31/95.

QAP20-2, Preparing, Reviewing, and Approving Scientific Notebooks, latest rev.

Shugar, Gershon J. and Ballinger, Jack T., 1990, Chemical Technicians' Ready Reference Handbook, Third Edition, McGraw-Hill, Inc.

SP472799, ES&H SOP Geochemical Research in the Dept. 6119 Colloid- and Sorption-Chemistry Laboratory, Bldg. 823, Room B45, 01/24/95.

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TOP-535, Calibration, Use, and Maintenance of pH Meters and Probes, latest rev.

TOP-536, Calibration, Use, and Maintenance of the Atomscan 25 Inductively Coupled Plasma Emission Spectrometer, latest rev.

TOP-537, Calibration, Use, and Maintenance of the ASAP 2000 BET Surface Area Analyzer, latest rev.

TOP-538, Calibration, Use, and Maintenance of the Model 5012 Carbon Dioxide Coulometer, latest rev.

TOP-539, Calibration, Use, and Maintenance of the N4MD Sub-Micron Particle Analyzer, latest rev.

TOP-540, Calibration, Use, and Maintenance of the Delsa 440 Electrophoretic Mobility Analyzer, latest rev.

TOP-541, Calibration, Use, and Maintenance of Eppendorf Model 4810 Autoclavable Pipettes, latest rev.

TOP-542, Calibration, Use, and Maintenance of Balances, latest rev.

TOP-543, Labeling, Tracking, and Shipping of Samples and Items, latest rev.

Table 1: Recipes for Synthetic Culebra Brines

	AISinR	H-17 Brine	VPX25	VPX26	VPX27	VPX28
Salt	Grams for 1 L	Grams for 1 L	Grams for 1 L	Grams for 1 L	Grams for 1 L	Grams for 1 L
H_3BO_3	0.1731					
$Na_2B_4O_7$			0.1201	0.1223	0.1238	0.1275
$Na_2B_4O_7 \bullet 10H_2O$		0.3792				
NaBr		0.0979	0.03271	0.0291	0.03129	0.02794
$NaHCO_3$	0.1495		0.07902	0.08492	0.08182	0.08392
$CaCl_2$	1.90	3.2108				
$CaCl_2 \bullet 2H_2O$			3.210	3.052	3.147	3.063
KCl	0.6103	2.2881				
K_2SO_4			0.7175	0.742	0.7175	0.7063
$MgCl_2 \bullet 6H_2O$	4.37	15.0562				
$MgSO_4$			2.248	2.074	2.228	2.094
NaCl	28.19	131.2	28.81	29.61	29.13	29.34
Na_2SO_4	11.31	10.6459	6.596	7.668	7.048	7.910

Table 2: Expected Compositions Based on Recipes in Table 1

Solute	AISinR	AISinR	H-17 Brine	H-17 Brine
	ideal	from recipe	ideal	from recipe
B (g/L)		0.0316		0.076
Br (g/L)				0.043
C (g/L)				0.050 HCO3
Ca (g/L)		0.6854		1.159
Cl (g/L)		20.130		88.000
K (g/L)		0.321		1.200
Mg (g/L)		0.5226		1.800
Na (g/L)		14.792		55.113
SO4 (g/L)		2.552		7.2
pH	7.46			

Table 3: Expected Compositions Based on Recipes in Table 1

Solute	VPX25	VPX25	VPX26	VPX26	VPX27	VPX27	VPX28	VPX28
	ideal	from recipe	ideal	from recipe	ideal	from recipe	ideal	from recipe
B (g/L)	0.0258	0.0258	0.0263	0.0263	0.0266	0.0266	0.0274	0.0274
Br (g/L)	0.0254	0.0254	0.0226	0.0226	0.0243	0.0243	0.0217	0.0217
C (g/L)	0.0113	0.0113	0.01214	0.01214	0.0117	0.0117	0.0120	0.0120
Ca (g/L)	0.875	0.875	0.832	0.832	0.858	0.858	0.835	0.835
Cl (g/L)	18.9	19.0	19.3	19.4	19.2	19.2	19.4	19.3
K (g/L)	0.322	0.322	0.333	0.333	0.322	0.322	0.317	0.317
Mg (g/L)	0.454	0.454	0.419	0.419	0.450	0.450	0.423	0.423
Na (g/L)	13.1	13.5	13.8	14.2	13.3	13.8	13.6	14.2
SO4 (g/L)	6.65	6.65	7.25	7.25	6.94	6.94	7.41	7.41
pH	7.65		7.69		8.10		8.09	